priority application was submitted and the present Application would be in condition for allowance.

As it is believed that the application is in condition for allowance, a favorable action and a Notice of Allowance are respectfully requested.

Applicants believe no fee is due at this time. However, the Commissioner is hereby authorized to deduct any deficiency or credit any overpayment to Deposit Account No. 19-3140.

Respectfully submitted,

Date: 10/31/05

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Customer No. 26263
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT : Yasuhito INAGAKI, et al.
APPLICATION No. : 09/905,662 Group Art Unit : 1746
FILING DATE : July 13, 2001 Examiner :Michail Komakov
TITLE : SUBSTRATE CLEANING METHOD AND
SUBSTRATE CLEANING APPARATUS

Hon. Commissioner of Patents and Trademarks,
Washington, D.C. 20231

SIR:

CERTIFIED TRANSLATION

I, Takashi Narita, am an official translator of the Japanese language into the English language and I hereby certify that the attached comprises an accurate translation into English of Japanese Application No. 2000-240134, filed on August 8, 2000.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

October 25, 2005

Date

Takashi Narita

Takashi Narita

[Document Name]	Patent Application
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[Filing Date]	August 8, 2000
[To]	Hon.Commissioner, Patent Office
[IPC]	H01L 21/304
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[Priority Right based on a Prior Application]

[Application Number] P2000-214974

[Date of Application] July 14, 2000

[Indication of Charge]

[Number of Prepaid Ledger] 019530

[Amount] 21,000 yen

[List of Document]

[Document]	Specification	1
[Document]	Drawing	1
[Document]	Summary	1

[General Power of Attorney Number] 9707387

[Need of Proof] Yes

[Document Name] Specification

[Title of the Invention] Substrate Cleaning Method and Substrate Cleaning Apparatus

[Claims]

[Claim 1]

A substrate cleaning method in which when a substrate is cleaned by using aqueous solution of ammonium fluoride and/or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid, at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the cleaning liquid with the elapse of using time of the cleaning liquid.

[Claim 2]

The substrate cleaning method according to claim 1, wherein the concentration of components of the cleaning liquid is detected and at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the cleaning liquid in accordance with the obtained result.

[Claim 3]

A substrate cleaning apparatus in which a substrate is cleaned by using aqueous solution of ammonium fluoride and/or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid, said substrate

cleaning apparatus comprising:

a substrate cleaning bath for accommodating the cleaning liquid; and

a feeding means for additionally feeding at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride to the substrate cleaning bath.

[Claim 4]

The substrate cleaning apparatus according to claim 3, further comprising a detecting means for detecting the concentration of components of the cleaning liquid, wherein at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the substrate cleaning bath by the feeding means in accordance with the result obtained in the detecting means.

[Detailed Description of the Invention]

[0001]

[Industrial Field of the Invention]

The present invention relates to a substrate cleaning method and a substrate cleaning apparatus using aqueous solution of ammonium fluoride or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid, and further relates to a novel substrate cleaning method and a novel substrate cleaning apparatus developed for the purpose of uniformly cleaning in a stable way and reducing an amount of use of the cleaning liquid.

[0002]

[Description of the Related Art]

The aqueous solution of ammonium fluoride (including the arbitrary mixture of hydrofluoric acid and ammonia or liquid having a surfactant) is mixed with hydrofluoric acid and the mixture is frequently used in a semiconductor or LCD producing process for the purpose of cleaning or etching a semiconductor (mainly, a silicon oxide film) substrate or a glass substrate.

[0003]

In these fields, to reduce the weight of a product, miniaturize a product and lower consumed electric power, a microfabrication technique of higher integration degree has been demanded. Accordingly, in cleaning the substrate by the aqueous solution of ammonium fluoride or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid, a more highly accurate process has been desired.

[0004]

[Problems to be Solved by the Invention]

In the cleaning or etching process, since chemical components (NH_4F, HF) in the cleaning liquid or water change (evaporate) with the elapse of time, an etching rate undesirably changes (increases) relative to the silicon oxide film or the glass substrate.

[0005]

This is caused from a phenomenon that during the use of the cleaning liquid, the concentration of the components of hydrofluoric acid in the cleaning liquid gradually increases with the elapse of time. Under the present condition, the cleaning liquid is frequently exchanged to meet the change of the concentration of various kinds of components in the cleaning liquid.

[0006]

However, in this measure, since an extremely large quantity of cleaning liquid needs to be used [especially, since the cleaning liquid including ammonium fluoride is employed under a state of high concentration as high as several tens % (for instance, about 40 % by weight), an amount of chemical consumed for each liquid exchange is more than that of other cleaning liquid that is ordinarily used under a concentration of about several %]. Consequently, an amount of use of ammonium fluoride or hydrofluoric acid (the cost of chemicals) is increased.

[0007]

Further, when the cleaning liquid is completely used, a waste water treatment as shown in Fig. 10 is necessary. In this case, a large quantity of resources (waste water treatment agent) is consumed, and accordingly, a large quantity of waste (waste water and sludge) is generated (see Fig. 11).

[0008]

Fig. 10 explains effluent treatment processes of the cleaning liquid. Effluent generated from a cleaning bath 81 is carried to a pH adjusting bath 82 in

which the effluent is neutralized by, for instance, 20 % calcium hydroxide solution. Then, the effluent is transferred to a coagulo-sedimentation bath 83 and subjected to coagulation and sedimentation by chemicals such as aluminum sulfate. Subsequently, the effluent is flocculated in a coagulating bath 84 by a polymeric flocculant such as polyacrylamide flocculant and subjected to sedimentation. After that, the effluent is discharged in the form of sewage or sludge.

[0009]

In the treatment processes as shown in Fig. 11, the 20 % calcium hydroxide of 2.0 kg, the 8 % aluminum sulfate of 0.3 kg and the polymeric flocculant of 1.6 kg are required relative to the 40 % aqueous solution of ammonium fluoride of 1.0 kg, and the sludge having 70 % solids content of 2.6 kg and sewage waste water of 2.3 kg are generated.

[0010]

In recent years, a global environmental problem is a worldwide interest and an environmental load when a substrate of a semiconductor or an LCD is produced has been considered to be a problem. Nowadays, as for the cleaning liquid, it has been socially eagerly requested not only to merely lower the cost, but also, to meet an environmental protection such the saving of resources, the decrease of waste, an environmental purification, etc.

[0011]

The present invention is proposed by considering the conventional

circumstances and it is an object of the present invention to provide a substrate cleaning method and a substrate cleaning apparatus that can uniformly clean a substrate in a stable way, save resources and reduce waste.

[0012]

[Means for Solving the Problems]

In order to achieve the above-described object, a substrate cleaning method of the present invention is characterized in that when a substrate is cleaned by using aqueous solution of ammonium fluoride and/or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid, at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the cleaning liquid with the elapse of using time of the cleaning liquid.

[0013]

Further, a substrate cleaning apparatus of the present invention in which a substrate is cleaned by using aqueous solution of ammonium fluoride and/or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid is characterized by having: substrate cleaning bath for accommodating the cleaning liquid; and a feeding means for additionally feeding at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride to the substrate cleaning bath.

[0014]

When the substrate is cleaned or etched by using the aqueous solution of ammonium fluoride and/or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as the cleaning liquid, at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the cleaning liquid in accordance with the elapse of using time of the cleaning liquid or the concentration of components of various kinds of chemicals in the cleaning liquid. Thus, the cleaning process of the substrate is homogenized and stabilized (an amount of etching is made to be uniform).

[0015]

In addition thereto, a frequency for a liquid exchange of the cleaning liquid is reduced to decrease an amount of use of the cleaning liquid. Furthermore, an amount of use of the chemicals necessary for treating the waste water of the cleaning liquid can be reduced and a quantity of generation of waste water and sludge discharged from a waste water treatment can be reduced.

[0016]

According to the present invention, the cleaning process of the substrate can be uniformly stabilized and the amount of use of the cleaning liquid or an amount of discharge can be reduced.

[0017]

[Embodiments of the Invention]

Now, a substrate cleaning method or a substrate cleaning apparatus to which the present invention is applied will be described in detail with reference to the drawings.

[0018]

According to the present invention, when a substrate is cleaned (or etched) by using aqueous solution of ammonium fluoride or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid, at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the cleaning liquid in accordance with the accumulated using time of the cleaning liquid or the concentration of components of various kinds of chemicals in the cleaning liquid.

[0019]

Fig. 1 shows a relation between an elapse of time and an etching rate relative to a thermal oxide film for the mixture of ammonium fluoride and hydrofluoric acid. The composition of the cleaning liquid is NH_4F (40%)/HF (50%) = 400/1. The temperature of the cleaning liquid is 25°C. The thermal oxide film is SiO_2.

[0020]

As understood from Fig. 1, the etching rate relative to the thermal oxide film is greatly increased with the elapse of time.

[0021]

When the substrate is cleaned by using the above-described cleaning liquid in such a way, the etching rate changes every moment. There is a very high correlation (proportional relation) between the etching rate and the elapse of time. This means that water or chemicals (NH_4F, HF) components in the cleaning liquid changes (evaporate) with the elapse of time, specifically, the water or an ammonia component in the cleaning liquid evaporates in a prescribed ratio and the concentration of an HF component (a component directly resulting from an etching operation of the thermal oxide film) increases in a prescribed ratio.

[0022]

Fig. 2 shows the change of the concentration of HF in the cleaning liquid in accordance with the elapse of time. Apparently, the concentration of HF increases in a prescribed ratio.

[0023]

From the above description, in the cleaning (etching) process of the substrate by the mixture of the aqueous solution of ammonium fluoride or hydrofluoric acid, the concentration of HF in the cleaning liquid needs to be uniformly and stably maintained. At this time, it may be said to be the most reasonable method to suitably feed the water apt to evaporate from the cleaning liquid.

[0024]

That is, when water is additionally fed as the time elapses, the rise of the

concentration of HF is suppressed so that a prescribed etching rate can be obtained. When the aqueous solution of ammonium fluoride is fed, the concentration of HF is also lowered so that the same effect can be anticipated.

[0025]

On the other hand, when ammonia is fed, HF is neutralized to produce ammonium fluoride. As a result, the concentration of HF in the cleaning liquid is suppressed. In the case of the ammonia water, both an effect by a dilution and an effect by neutralization can be expected.

[0026]

As a result, the yield of the substrate of a semiconductor or a liquid crystal can be improved and the frequency of liquid exchange can be reduced, so that the chemicals of the cleaning liquid or a waste water treatment agent can be saved and a quantity of generation of sludge or waste water can be reduced.

[0027]

Fig. 3 shows one structural example of a substrate cleaning apparatus to which the present invention is applied.

[0028]

The substrate cleaning apparatus includes a substrate treatment bath 1 for accommodating cleaning liquid such as the mixture of ammonium fluoride and hydrofluoric acid to clean a substrate and a circulation pump 2 for circulating the overflowing cleaning liquid to the substrate treatment bath 1. For instance, the

substrate as a member to be treated is accommodated in a substrate carrier and the substrate carrier is immersed in the substrate treatment bath 1 to clean (etch) the substrate.

[0029]

Here, it is characteristic that a constant delivery pump 3 for feeding water is provided in the substrate treatment bath 1 and a controller 4 controls water to be additionally fed.

[0030]

As described above, the concentration of a component of HF in the cleaning liquid increases in a prescribed ratio with the elapse of time and an etching rate relative to a thermal oxide film is greatly increased.

[0031]

Thus, in this substrate cleaning apparatus, the controller 4 controls the water to be additionally fed to the substrate treatment bath 1 from the constant delivery pump 3 to make the concentration of HF constant and the etching rate substantially constant with the elapse of time.

[0032]

Fig. 4 shows the change of the concentration of HF in accordance with the additional feeding of the water. Fig. 4 shows that the concentration of HF increasing with the elapse of time is returned to original concentration by additionally feeding water. The control of the concentration of HF by

additionally feeding the water results in the control of the etching rate. As shown in Fig. 5, the etching rate is lowered by additionally feeding the water.

[0033]

As for an amount of feeding of water and a water feeding timing, data as shown in Fig. 1 or Fig. 2 is taken to calculate water that evaporates with the elapse of time, so that the conditions of a most suitable amount of feeding of water and water feeding timing can be derived.

[0034]

Fig. 6 is a diagram showing the controlled state of the etching rate or the concentration of HF by the additional feeding of water. Water is intermittently additionally fed, and accordingly, the etching rate or the concentration of HF is maintained within a prescribed range.

[0035]

As a condition for feeding water, either a continuous feeding or an intermittent feeding may be employed. To constantly maintain a prescribed concentration, the continuous feeding is more preferable.

[0036]

In the substrate cleaning apparatus, the timing for additionally feeding water is controlled on the basis of the measured data. However, as shown in Fig. 7, a concentration measuring unit 5 may be provided to measure the concentration of circulated cleaning liquid and control the additional feeding of water in real time

on the basis of the information of the concentration.

[0037]

Specifically, the concentration of each of the components (ammonia, hydrofluoric acid, water, etc.) in the cleaning liquid is measured by the concentration measuring unit 5 and the measured results are transmitted to the controller 4 composed of a computer or a central monitoring unit. Then, after whether or not the water needs to be fed is decided and a necessary amount of feeding of the water is calculated, an instruction for feeding of the water is sent to a water feeding line (constant delivery pump 3). Then, whether or not the water is fed as instructed is recognized under the measurements by the concentration measuring unit 5.

[0038]

As a method for measuring the concentration of the components in the cleaning liquid, the measurements of a degree of absorption of a prescribed wavelength, an infrared/ultraviolet absorption spectrum, a refraction index, a specific gravity, a transmittance, an electric conductivity or the like may be used, or measuring units such as a Karl Fischer moisture titrator or a liquid (ion) chromatography or the like may be employed.

[0039]

Figs. 8 and 9 show an aqueous ammonia storage tank 6 provided for feeding aqueous ammonia in place of the constant delivery pump 3 for feeding

water.

[0040]

The aqueous ammonia is additionally fed in place of the water so that the concentration of HF is also effectively controlled and the etching rate is controlled to be constant.

[0041]

As for the feeding of ammonia, not only the aqueous ammonia, but also other suitable aqueous solution may be used. Further, ammonia gas may be employed. Otherwise, aqueous solution of ammonium fluoride may be used and ammonia and ammonium fluoride may be co-used.

[0042]

As described above, in accordance with the decision from the etching rate at each of the processing times or the concentration of various kinds of components, the water, the aqueous ammonia or the aqueous solution of ammonium fluoride is additionally fed so that the etching process by the cleaning liquid can be homogenized/stabilized (that is, an amount of etching relative to the oxide film is maintained to be constant). The cleaning liquid does not need to be frequently exchanged as in usual. Thus, the long life of the cleaning liquid can be realized and the frequency for the liquid exchange can be reduced to contribute to the decrease (saving of resources) of a quantity of consumption of the cleaning liquid and the decrease (saving of resources) of the waste water treatment agent required

for treating waste water of the cleaning liquid. Furthermore, the decrease of an amount of use of these chemicals can contribute to the decrease (the decrease of an amount of generation of waste) of an amount of the discharge of sludge or waste water generated during the waste water treatment.

[0043]

As apparent from the above, the present invention not only attempts to homogenize/stabilize a substrate process, but also contributes to a global environmental protection from the viewpoint of the saving of resources and the decrease of a quantity of generation of waste.

[0044]

[Effects of the Invention]

As described above, when the substrate is cleaned by the aqueous solution of ammonium fluoride and the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid, the process can be uniformly stabilized and the frequency for changing the cleaning liquid can be reduced by using the method and the apparatus of the present invention. Accordingly, the resources of the chemicals (the cleaning liquid, the waste water treatment agent) can be saved and the quantity of discharge of the sludge or the waste water caused thereby can be greatly reduced.

[Brief Description of the drawings]

[Fig. 1]

Fig. 1 is a characteristic view showing the relation between an elapse of time and an etching rate in cleaning liquid.

[Fig. 2]

Fig. 2 is a characteristic view showing the relation between an elapse of time and the concentration of HF in the cleaning liquid.

[Fig. 3]

Fig. 3 is a schematic view showing one example of a substrate cleaning apparatus to which the present invention is applied.

[Fig. 4]

Fig. 4 is a characteristic view showing the change of the concentration of HF when water is additionally fed.

[Fig. 5]

Fig. 5 is a characteristic view showing the change of the etching rata when water is additionally fed.

[Fig. 6]

Fig. 6 is a diagram showing the controlled states of the etching rate or the concentration of HF by additionally feeding the water.

[Fig. 7]

Fig. 7 is a schematic view showing another example of the substrate cleaning apparatus to which the present invention is applied.

[Fig. 8]

Fig. 8 is a schematic view showing one example of a substrate cleaning apparatus in which an aqueous ammonia storage tank is disposed.

[Fig. 9]

Fig. 9 is a schematic view showing another example of the substrate cleaning apparatus in which an aqueous ammonia storage tank is disposed.

[Fig. 10]

Fig. 10 is a diagram for explaining effluent treatment processes of the cleaning liquid.

[Fig. 11]

Fig. 11 is a diagram showing resources necessary for effluent treatments of the cleaning liquid.

[Description of the Numerals]

1 substrate treatment bath

2 circulation pump

3 constant delivery pump

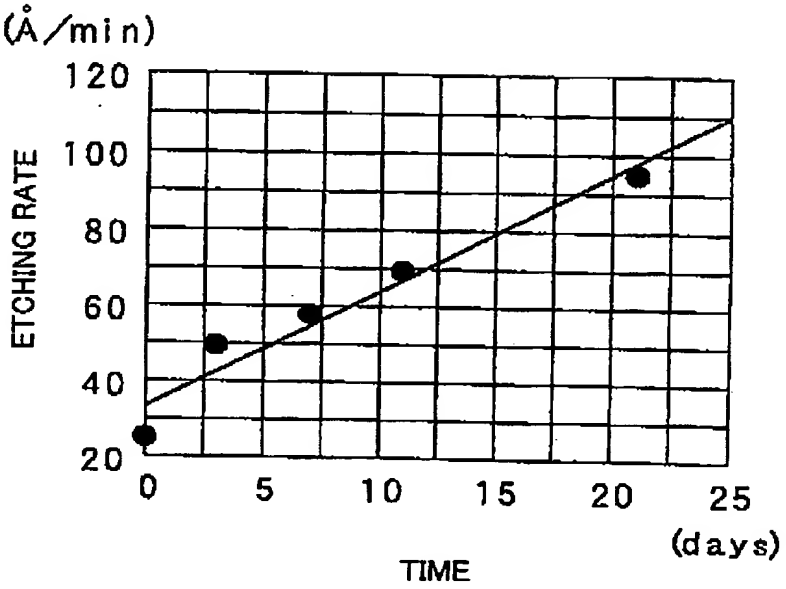
4 controller

5 concentration measuring unit

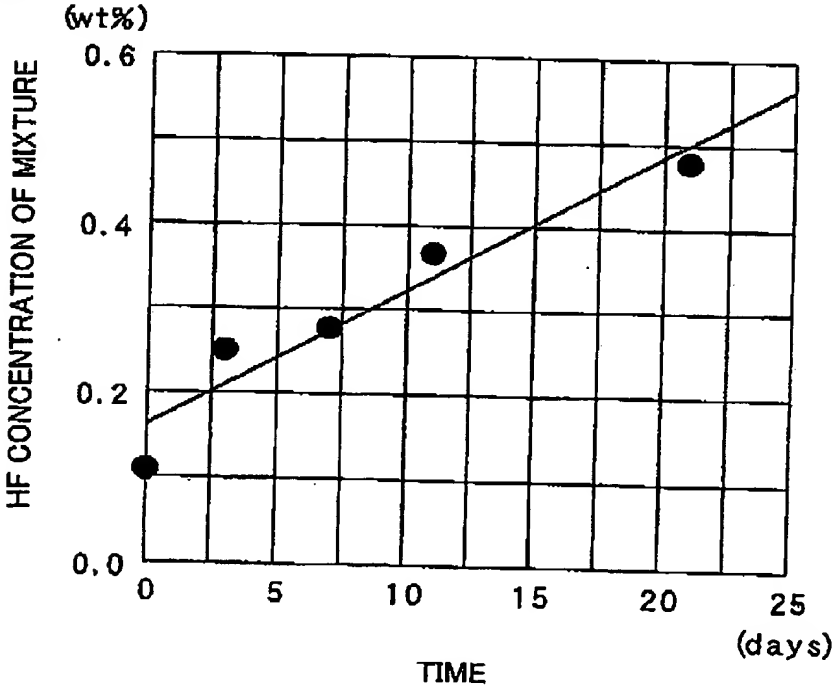
6 aqueous ammonia storage tank

[DOCUMENT NAME] DRAWING

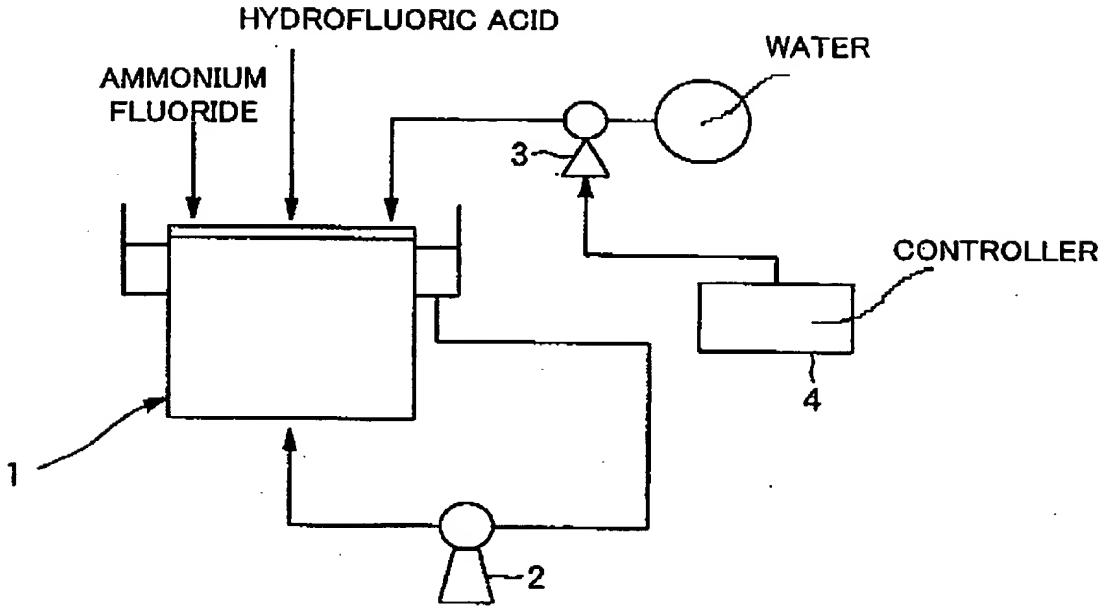
[FIG.1]



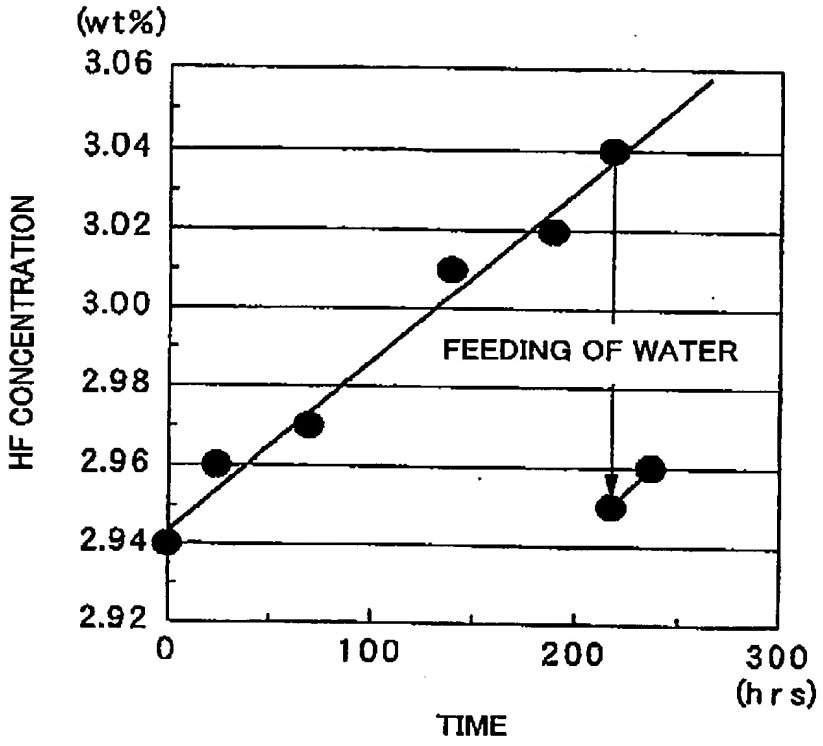
[FIG.2]



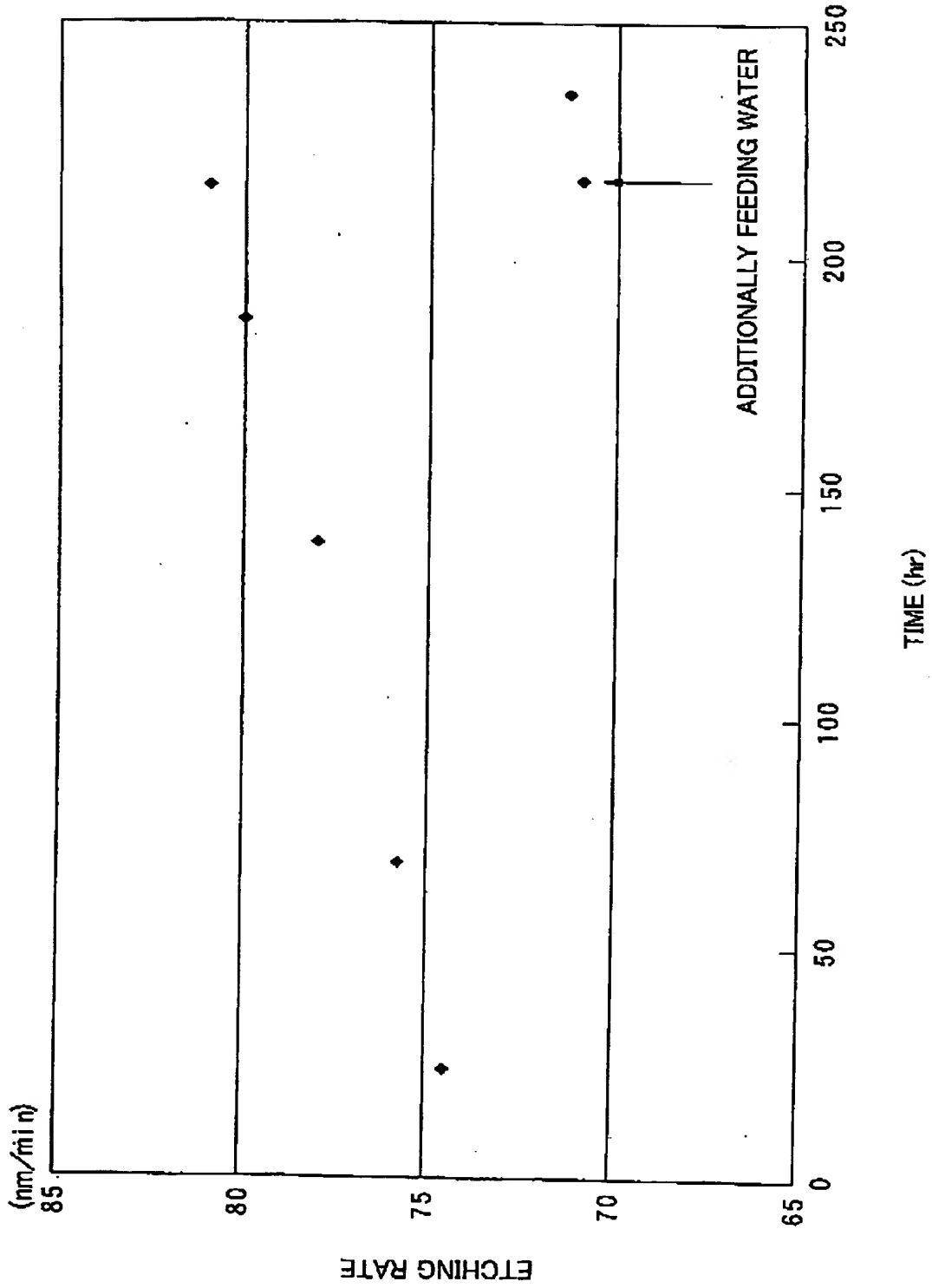
[FIG.3]


HYDROFLUORIC ACID
AMMONIUM FLUORIDE
WATER
3
CONTROLLER
4
1
2

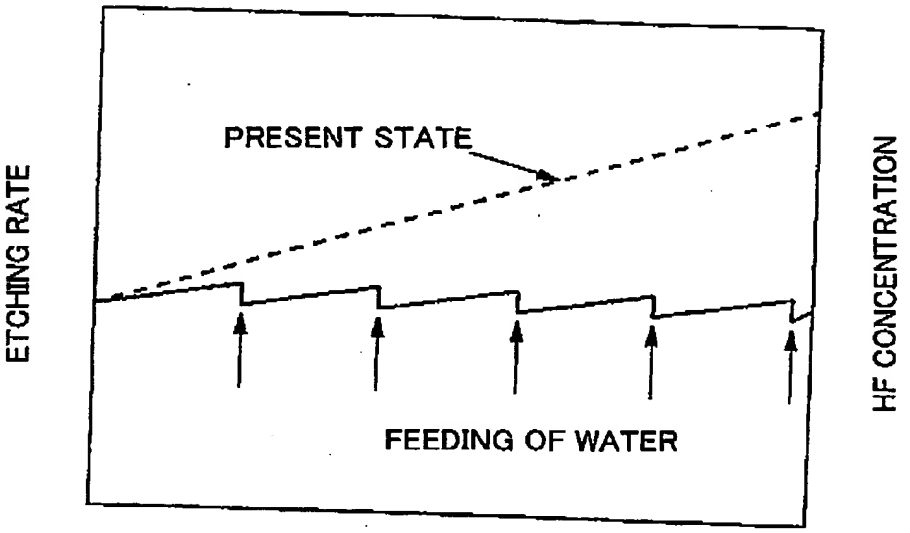
[FIG.4]


(wt%)
3.06
3.04
3.02
3.00
2.98
2.96
2.94
2.92
HF CONCENTRATION
FEEDING OF WATER
0
100
200
300
(hrs)
TIME

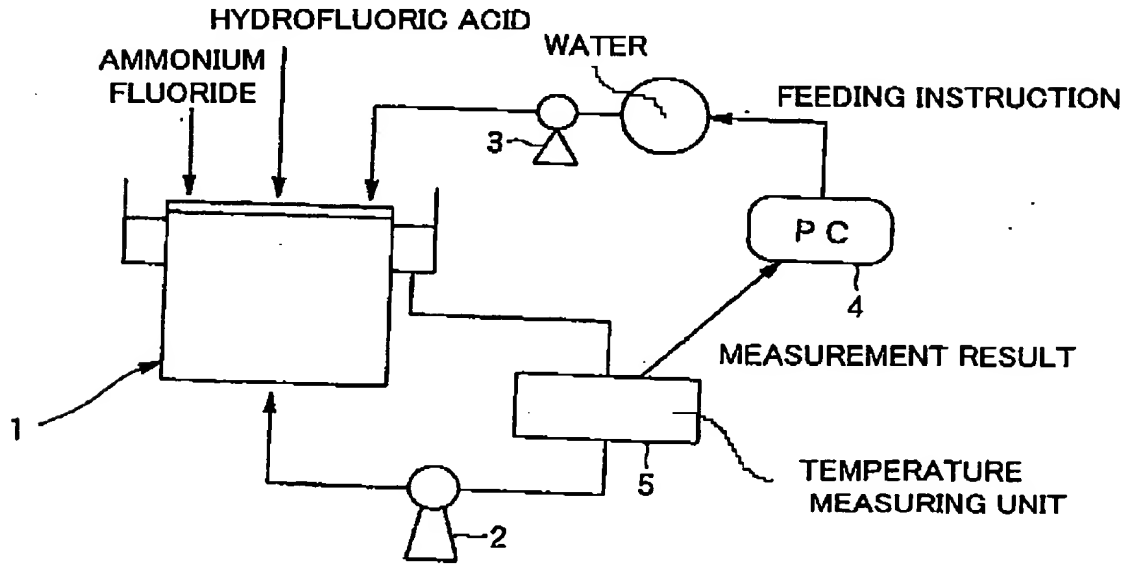
[FIG.5]


ETCHING RATE
(nm/min)
85
80
75
70
65
0
50
100
150
200
250
TIME (hr)
ADDITIONALLY FEEDING WATER

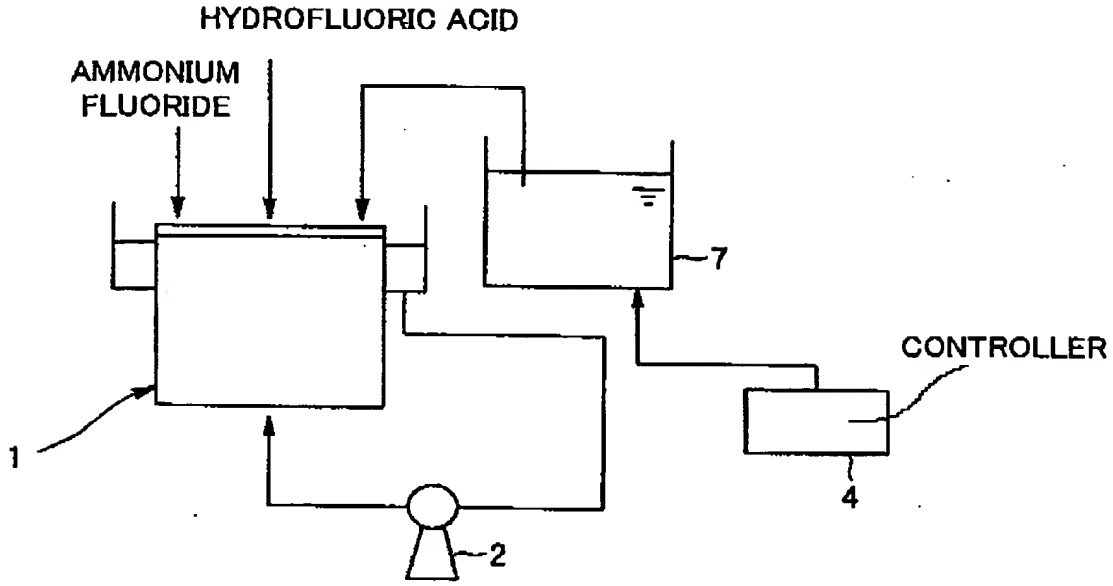
[FIG.6]


PRESENT STATE
ETCHING RATE
HF CONCENTRATION
FEEDING OF WATER

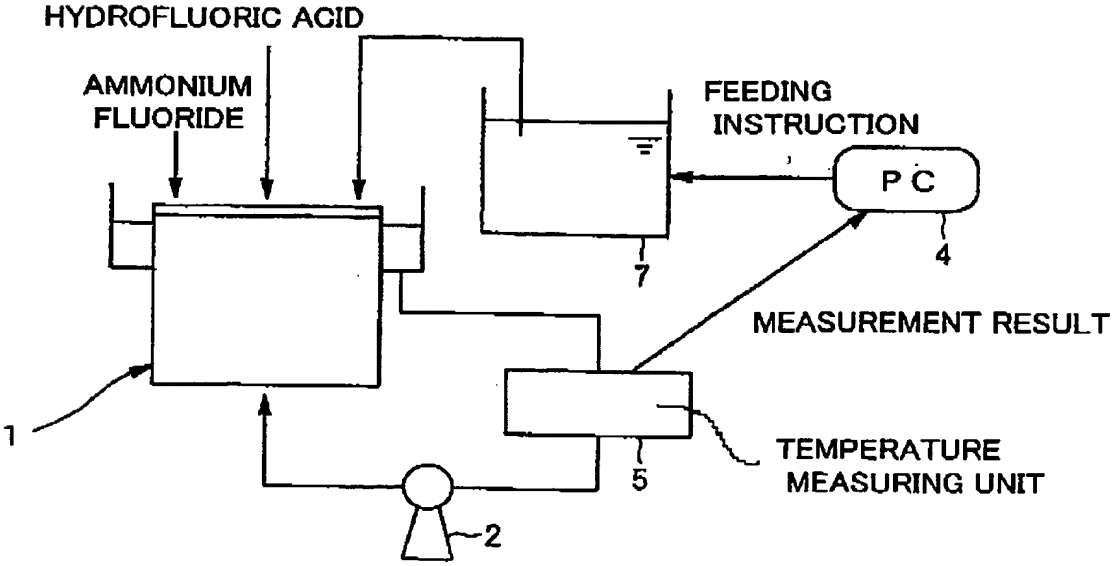
[FIG.7]


HYDROFLUORIC ACID
AMMONIUM FLUORIDE
WATER
FEEDING INSTRUCTION
3
PC
4
MEASUREMENT RESULT
1
5
TEMPERATURE MEASURING UNIT
2

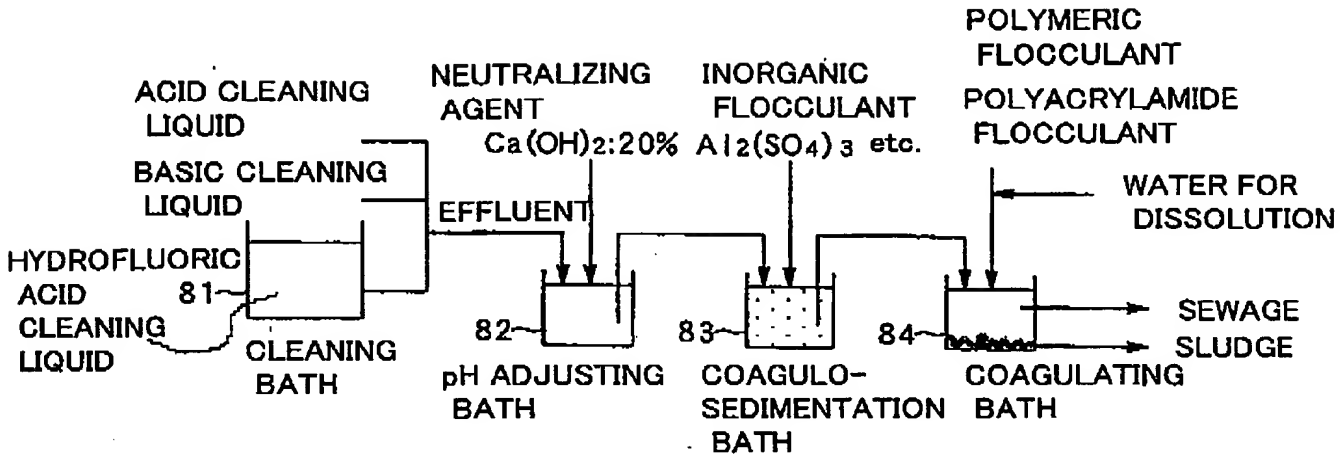
[FIG.8]


HYDROFLUORIC ACID
AMMONIUM FLUORIDE
7
CONTROLLER
1
4
2

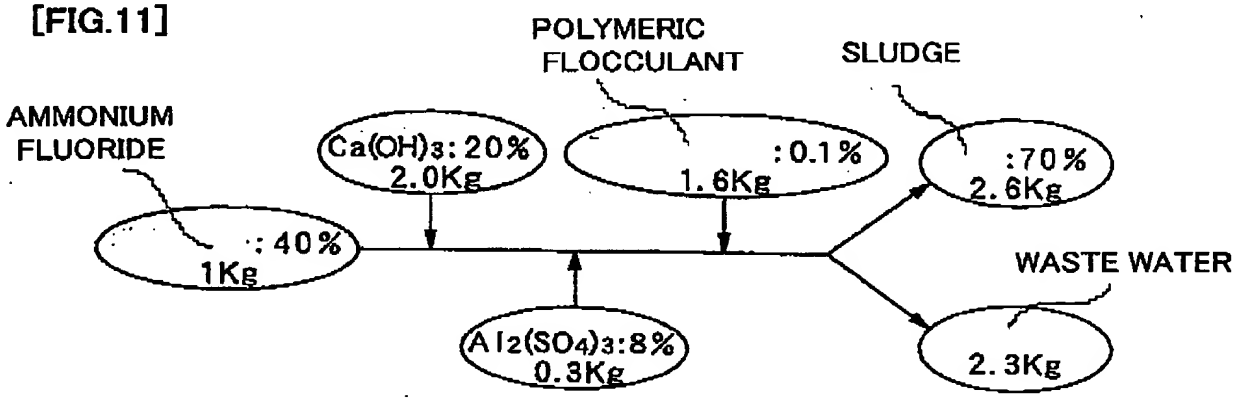
[FIG.9]


HYDROFLUORIC ACID
AMMONIUM FLUORIDE
FEEDING INSTRUCTION
P C
4
7
MEASUREMENT RESULT
1
TEMPERATURE MEASURING UNIT
5
2

[FIG.10]


ACID CLEANING LIQUID
BASIC CLEANING LIQUID
HYDROFLUORIC ACID CLEANING LIQUID
81
CLEANING BATH
NEUTRALIZING AGENT
Ca(OH)2:20%
EFFLUENT
82
pH ADJUSTING BATH
INORGANIC FLOCCULANT
Al2(SO4)3 etc.
83
COAGULO-SEDIMENTATION BATH
POLYMERIC FLOCCULANT
POLYACRYLAMIDE FLOCCULANT
WATER FOR DISSOLUTION
84
SEWAGE SLUDGE
COAGULATING BATH

[FIG.11]


AMMONIUM FLUORIDE
:40%
1Kg
Ca(OH)3:20%
2.0Kg
POLYMERIC FLOCCULANT
:0.1%
1.6Kg
Al2(SO4)3:8%
0.3Kg
SLUDGE
:70%
2.6Kg
WASTE WATER
2.3Kg

[Name of Document] Abstract

[Abstract]

[Object] To uniformly and stably clean substrate, save resources and reduce waste at the same time.

[Means for Solving Problem] When a substrate is cleaned by using aqueous solution of ammonium fluoride or the mixture of the aqueous solution of ammonium fluoride and hydrofluoric acid as cleaning liquid, at least one kind of material selected from water, ammonia, aqueous ammonia and the aqueous solution of ammonium fluoride is additionally fed to the cleaning liquid with the elapse of using time of the cleaning liquid. At this time, a necessary amount of feeding of the material corresponding to the elapse of time is calculated on the basis of measured data and controlled. Otherwise, the concentration of components in the cleaning liquid may be detected to additionally feed the material in accordance with the obtained result.

[Selected Drawing] Fig. 3